

Interactive comment on “Oxalic acid as a heterogeneous ice nucleus in the upper troposphere and its indirect aerosol effect” by B. Zobrist et al.

B. Zobrist et al.

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The authors would like to thank anonymous referee #3 for his/her constructive comments. We have addressed the referee's concerns point-by-point below.

Comment(1):

We use the term "atmospheric conditions" to refer to a temperature and aqueous solution (or water activity) range typical for the upper troposphere. To cover these conditions, we have performed ice nucleation experiments not only with pure oxalic acid solutions but also in the presence of other solutes (malonic acid, sulfuric acid, sodium chloride, ammonium bisulfate). With these experiments we cover a temperature range from 204–238 K, which corresponds with the one of the microphysical box model (200–230 K).

There is indeed just little known about the oxalic acid concentration in the upper troposphere. However the best available data for the size distribution and concentration of the oxalic acid have been taken as the input data for the microphysical box model (Zaizen et al., J. Meteor. Soc. Japan, 82, 11478211;1160, 2004 and Narukawa et al., Tellus, 55B, 7778211;786, 2003). The occurrence of the oxalic acid in the upper troposphere is also confirmed by the single particle measurements (PALMS measurements) of this study. We have therefore a good experimental basis to apply our results to the microphysical and global models.

Comment(2):

For instance, what about deposition to other solid surfaces, e.g. minerals, and subsequent heterogeneous crystallisation.

Of course, deposition ice nucleation to other solids like minerals is possible. However, the three prerequisites formulated on page 3573 do apply only to water soluble organic substances. We have reworded the paragraph accordingly.

What about deposition nucleation directly to solid oxalic acid particles?

We believe that the occurrence of dry OAD particles in the atmosphere is unlikely, see below. In addition, laboratory measurements by Prenni et al. (J.Phys.Chem.A 105, 11240, 2001) and Parsons et al. (JGR 109, D06212, 2004) indicate, that dicarboxylic acids do not appear to be very efficient deposition ice nuclei. The measurements by Prenni et al. include experiments on oxalic acid particles.

On the other hand, they mention that oxalic acid can also be formed as a secondary product from organic precursors. I suspect this also involves gas-phase reactions.

No. The modelling study by Ervens et al. concludes that oxalic acid is the endpoint of the aqueous liquid phase oxidation of organic compounds. We will add several sentences to the manuscript to make this more clear.

Can one really exclude from the sparse knowledge and data basis that oxalic acid [...] act as an ice nucleus in different modes?

Given the diversity of substances in the atmosphere it is basically impossible to investigate all potential organic ice nuclei in every mode. Therefore, we did focus on the substances and modes that we consider to be the most likely in the atmosphere, given the restricted evidence from field data and modelling studies. This leads to the three criteria given on page 3573. In our opinion this list of criteria allows to define suitable and likely candidates for organic IN, but is not to mean to be exclusive, i.e., we can not completely exclude oxalic acid acting in modes other than immersion freezing, but we believe that it is unlikely. We have revised the paragraph introducing the criteria list, and have made several other changes and additions to this paragraph (see above).

Comment(3):

Is the dashed curved scaled vs. the solid?

The dashed and the solid curves in Figure 1 show the raw data; they are not scaled, but only shifted vertically for clarity.

At least the homogeneous nucleation rate is a steep function of the temperature. Shouldn't the DSC peaks therefore be more narrow? How compares the peak width of the pure water runs with the oxalic acid runs? In other words, can one conclude from the peak width for the dependence of the nucleation rate on temperature (as mentioned in the appendix) or is the peak width mainly determined by instrument parameters?

The shape of the peaks in a DSC curve depends on both sample properties (droplet size distribution, sample mass, nucleation rate characteristics $\partial J/\partial T$ of the investigated sample) as well as instrumental parameters (cooling rate, latent heat transport, instrument sensitivity). At larger cooling rates, the peak width is more sensitive to

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instrument parameters as the observed width in Fig.1 of 18 K is not due to nucleation events occurring over this temperature range. Rather, the latent heat that is released in the onset region of the freezing peak needs time to diffuse away from the sample to the cooling block of the DSC. Nevertheless, the peak width of the homogeneous freezing peak and the heterogeneous freezing peak shown in Fig.1 is identical within experimental uncertainty, indicating no major changes in the nucleation rates. They are also nearly identical to the peak observed when a pure water sample freezes homogeneously. When the cooling rate is reduced to 1 Kmin^{-1} the width of the peak is reduced to $\sim 5 \text{ K}$ for both freezing processes. More important than the peak width is the onset and onset slope of the peaks as these are more closely related to the nucleation rate of the droplets. Again, they are identical within experimental uncertainty, indicating that $\partial(V \cdot J_{hom})/\partial T$ and $\partial(A \cdot J_{het})/\partial T$ are very similar for the two processes.

Can the fraction of OAD particles acting as heterogeneous IN in the second cycle be estimated from the data?

The fraction of OAD particles not acting as heterogeneous IN in the second cycle is negligible as no clear second freezing peak (corresponding to the homogeneous freezing temperature) is found in the second freezing cycle. When we varied the conditioning temperature to very close to the melting temperature of oxalic acid dihydrate or even above it for very short moments, either a shoulder or a second peak was observed. The magnitude of that second peak clearly correlated with how close the sample was heated to the melting temperature.

Can the definition of the 8217;freezing point8217; be indicated in Figure 1? The freezing point given for the homogeneous run (solid red line) is different from that in Table 1. Please check for consistency.

The freezing point is defined as the temperature at the onset of the DSC peak. We will indicate this in Fig.1 for clarity. The value in Table 1 represents a mean value

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of several individual freezing points, while that in Fig.1 is the actual value for this particular experiment. We will indicate the fact that the tables shows mean values as well as their uncertainties in the captions to both tables.

Comment(4):

The difference between the experimental homogeneous freezing points and the prediction (solid line) of water-activity-based nucleation theory (Koop et al. 2000) is only very small: the largest deviation occurs for a 30wt% malonic acid sample that froze at 217.8 K and amounts to a difference in a_w of 0.018, i.e. a relative difference of 1.98%. This is well within the uncertainty of our knowledge of water activities in supercooled aqueous malonic acid solutions, as it is almost equal to the experimental uncertainty of $\pm 1\%$ in measured water activities of malonic acid system above the ice melting point curve given in Braban et al. (2003). In addition, this deviation is also well within that of all other solutes used to derive the black solid line (see Fig.9 in Koop, Z.Phys.Chem. 218, 1231–1258, 2004; in that paper, it is also shown, how a small temperature dependence in a_w affects the freezing point of the solution.) Therefore, we feel that the statement by the referee that “... *the homogeneous freezing points are rigorously shifted to be in agreement with the homogeneous freezing formalism suggested by Koop et al. (2000).*” is exaggerated.

Furthermore, the correction was not applied for evaluating the data; in fact δa_w as shown in Fig.2a was obtained directly from the raw data according to Equation 3, and the resulting δa_w was used in the microphysical box model.

We did show the shifted data in Fig.2b in order to illustrate the extremely consistent picture that results for the water activity dependence of heterogeneous ice nucleation on OAD in all investigated solutions, when the scatter with respect to homogeneous nucleation (which we believe is due the uncertainty in a_w) is removed. In our opinion Fig.2b strongly supports the fact that the water-activity-based approach is also

applicable to heterogeneous ice nucleation in the immersion mode, which is also supported by two other laboratory studies (Zuberi et al. 2002, Archuleta et al. 2005). As the surface area of the OAD in all solutions is very similar we propose that along a line of constant $\Delta a_{w,\text{het}}$ also the heterogeneous ice nucleation rate coefficient remains constant. This is completely consistent with the water-activity-based nucleation theory for homogeneous nucleation in which the homogeneous nucleation rate coefficient remains constant along a constant $\Delta a_{w,\text{hom}}$ line, independently of temperature (Koop et al. 2000).

In conclusion, within experimental uncertainty, there is no apparent inconsistency between the measurements, water-activity-based nucleation theory and the parameterization applied in the box model.

We will add a paragraph to the manuscript in order to discuss our approach more clearly .

Comment(5):

The vapor pressure of a pure oxalic acid dihydrate crystal is equal to that of a solution droplet that contains embedded oxalic acid dihydrate crystals that are in equilibrium with the solution. Because of the lack of data, we estimate the growth time by assuming that oxalic acid nano-crystals have a vapor pressure of 0, which only provides a lower limit. However, at this stage we wanted to assess whether such a Bergeron-Findeisen like process takes place under upper tropospheric conditions rather than calculate exact growth rates. More data on the composition of the upper tropospheric aerosol properties are required in order to improve this estimate.

Comment(6):

The droplet size distribution of a large number (≥ 30) of individual emulsion have been analyzed with an optical microscope. In these tests only very small differences

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in the size distribution were observed. In addition, we have checked the reproducibility of the freezing temperatures of emulsion containing aqueous droplets of the same concentrations and found only very small deviations, with a maximum deviation of ± 0.3 K. For example, the freezing temperatures of 7 measurements with 5 differently prepared emulsions of pure water droplets varied by less than 0.2 K. Similar deviations were observed with the emulsion droplets containing inorganic or organic solutes. We have added sentences to the captions of both tables to explicitly state the uncertainty/reproducibility of the freezing temperatures T_{f1} and T_{f2} given in the tables.

Comment(7):

At the beginning of Section 4 it is stated that the experimental results may be parameterized with water-activity based nucleation theory for model application. However, nucleation theory was not yet applied up to this point. Strictly speaking it was just shown that heterogeneous freezing occurs at a somewhat higher mean temperature.

The referee is correct with his/her statement that at this point of the paper it is not clear how we deduce heterogeneous nucleation rates from our data, as this information is given only in the appendix. We have revised the first paragraph in section 4 accordingly and moved it to the end of section 3.3: "So far it was shown that oxalic acid may act as a immersion mode ice nucleus and that the effect of OAD on freezing temperature can be parameterized using water-activity. In appendix B, we use this information to estimate the heterogeneous ice nucleation rate coefficient for immersion nucleation and how it can be parameterized for inclusion into a microphysical box model. In the following section, the occurrence of OAD in the UT and its possible influence on the microphysical and radiative properties of cirrus clouds are investigated."

Comment(8):

We agree that our statement might lead to a misunderstanding, since there is clearly a dependence on cooling rate (this is shown in Fig.4), and indeed the effect might

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be slightly larger at lower cooling rates. However, such small cooling rates are rather scarce in the upper troposphere (see dashed black line in Figure 4).

We have rephrased the paragraph in order to avoid any misunderstanding:

“For a given IN number density, the reduction in n_{ice} when compared to homogeneous nucleation is largest at cooling rates greater than that cooling rate, at which $n_{ice,hom}$ is approximately equal to IN number density.”

All minor comments and typos have been corrected:

p.3572, l.6: we have replaced “2-5” by “2 and 5”

p.3577, l.22: the word “single” has been added.

p.3579, l.7: “highly” has been removed

p.3582, l.21: we have added “...–by less than 2% in a_w –...”

p.3584, l.12: Yes, peak 89 was also observed in the lab.

p.3589, l.22: We have reworded the sentence: “There is ample evidence that oxalic acid is contained in upper tropospheric aerosols (Narukawa et al., 2003a, and this study) and it is very likely that...”

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 3571, 2006.

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